Development of Porous Layered Magnets toward the Control of Their Magnetic Functionality with Chemical Stimuli

（別紙様式５）

論　文　内　容　要　旨

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氏　　名	Zhang　Jun　(張　俊)	提出年	令和元年
学位論文の 題　　目	Development of Porous Layered Magnets toward the Control of Their Magnetic Functionality with Chemical Stimuli （化学的刺激による磁気機能性制御に向けた多孔性層状磁石の開発）		

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Chapter 1. Introduction

The molecule-based magnet has been attracted wide attention for the potential applications as sensor, memory, chemical switch, and quantum computing. A material showing a reversible magnetic change in response to chemical stimuli (solvents or gases) is desirable in the both fields of metal-organic frameworks/porous coordination polymers (MOFs/PCPs) and molecule-based magnets. Meanwhile, a change in the intrinsic spin state in MOF inevitably brings a significant change in its magnetic behavior. So, the electronic state modulation (ESM) in an electronically-correlated coordination lattice is an efficient strategy to obtain materials showing a drastic change in their magnetism, which will be realized via the dynamic control of intra-lattice electron transfer/charge transfer in response to external stimuli. In order to obtain such “charge-flexible magnets”, we have focused on a class of donor/-acceptor MOF (D/A-MOF) comprising from carboxylate-bridged paddlewheel-type

diruthenium(II,II) complex ([$Ru_2^{II,II}$]) as an electron donor (D) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) as an electron acceptor (A) with a two-dimensional (2D) layered structure of D_2A composition. These D/A-MOFs demonstrate four distinct types of electronic states: neutral state (N; $D^0{}_2A^0$), one-electron transferred state (1e-I; $D^{0.5+}{}_2A^{-}$), two-electron transferred state (2e-I; $D^{+}{}_2A^{2-}$), and partially electron transferred state (1.5e-I; $D^{0.75+}{}_2A^{1.5-}$). Furthermore, the void space is existing between the layers, which is great advantage for the accommodation of guest molecule. And hence, we strongly anticipate in the utilization of such space as a powerful tool to control the electronic states of D/A-MOFs by chemical stimuli, resulting in the switch of the magnetic properties. In this thesis, several examples of reversible magnetic changes closely associated with ESM as well as structural modifications realized by guest insertion/removal cycles will be discussed.

Chapter 2. Electronic states modulation induced T_c switching via solvent in a porous layered magnet

The reversible magnetic switch through ESM by solvation/desolvation cycles of the solvent vapor as chemical stimulus was demonstrated in the compound [{Ru_2(2,3,5-Cl_3PhCO_2)$_4$}$_2$(TCNQMe_2)]·4DCM (**1**; 2,3,5-Cl_3PhCO_2^- = 2,3,5-trichlorobenzoate; TCNQMe_2 = 2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane, DCM = dichloromethane), where [Ru_2(O_2CPh-2,3,5-Cl_3)$_4$] ([Ru_2]) is an electron-donor (D) and TCNQMe_2 is an electron-acceptor (A). The solvated phase **1** had a 1e-I state. Strong intralayer antiferromagnetic couplings between [$Ru_2^{II,II}$] with S = 1 or [$Ru_2^{II,III}$]$^+$ with S = 3/2 and TCNQ$Me_2^{\bullet-}$ with S = 1/2, as well as ferromagnetic interlayer interactions, induced long-range ferrimagnetic ordering at T_c = 101 K. While electronic state of desolvated phase (**1-dry**) thermally fluctuated and eventually provided a 1.5e-I state as the ground state. The T_c in **1-dry** was 34 K because of the presence of diamagnetic TCNQMe_2^{2-} in some parts of the framework. A large T_c variation with $\Delta T_c \approx 70$ K was reversible. The geometry of TCNQ moiety was affected by the solvent accommodation, which induced ESM upon solvation/desolvation cycle.

Chapter 3. Host-guest interaction induced T_c switching in a porous layered magnet

[{Ru_2(*m*-FPhCO_2)$_4$}$_2$TCNQ(OMe)$_2$]·*n*DCE (**3-*n*DCE**; *m*-FPhCO_2^- = *meta*-fluorobenzoate; TCNQ(OMe)$_2$ = 2,5-dimethoxyl-7,7,8,8-tetracyanoquinodimethane; DCE = 1,2-dichloroethane) undergoes ESM via three distinct states of 2e-I state for **3-4DCE**, 1.5e-I state for **3-*n*DCE** ($n \leq 1$), and 1e-I state for **3** depending on the degree of solvation. Resolvations from **3** only stabilize **3-DCE**, allowing ESM between 1.5e-I and 1e-I, as well as the change in ferrimagnetic T_c between 30 K and 88 K, respectively. This behavior is similar to that observed in **1** in chapter 2, though, structural analysis indicated that the crystal structure of **3-*n*DCE** and **3** is almost identical; the ESM between **3-*n*DCE** and **3** cannot be explained by the structural factor. Whereas, theoretical calculations based on density functional theory indicated that the hydrogen-bond between host framework and crystallization solvent suppresses an electron-donation ability of D unit, and hence, 1e-I state was stabilized in **3-DCE** while 1.5e-I state was realized in **3**. Namely, weak host-guest interaction, such as hydrogen bond, plays important role for ESM in this compound.

Chapter 4. Solvent dependence induced magnetic phases switching in a porous layered magnet

The achieved magnetic changes until the previous chapters still remains unsatisfactory because they are just the variation in T_c, and not a change of magnetic phase itself. The first multiple switches of magnetic phases was successfully achieved in [{Ru_2(2,4-F_2PhCO_2)$_4$}$_2$TCNQ(OEt)$_2$] (**4**; 2,4-F_2PhCO_2^- = 2,4-difluorobenzoate;

$TCNQ(OEt)_2$ = 2,5-diethoxy-7,7,8,8-tetracyanoquinodimethane). Desolvated-phase **4** showed temperature-induced charge transfer around 380 K between 1e-I state (high temperature phase) and 2e-I state (low temperature phase), and hence, **4** was paramagnet (no long-range magnetic order) down to cryogenic temperature. Meanwhile, exposing **4** to various kind of solvent vapors such as benzene (PhH), *p*-Xylene (PX), DCE, DCM, and carbon disulfide (CS_2) gave the corresponding solvent-adsorbed phases (**4-solv**s), which revealed 1e-I state with strong intra-layer antiferromagnetic coupling between $[Ru_2^{II,II}]$ (S = 1) or $[Ru_2^{II,III}]^+$ (S = 3/2) and $TCNQ(OEt)_2^{\bullet-}$ (S = 1/2). The ferromagnetic inter-layer interactions for **4-PhH**, **4-PX**, **4-DCE**, and **4-DCM** induces ferrimagnetic phase transition temperature (T_c) of 88, 92, 74, and 70 K, respectively, while antiferromagnetic inter-layer interaction is operative in **4-CS_2**, resulting in antiferromagnetic phase transition with Néel temperature (T_N) of 78 K. The magnetic phases in this series of pseudo-polymorphs can be reversibly and multiply switched between paramagnet and ferrimagnet/antiferromagnet through solvation and desolvation process.

Chapter 5. CO_2-adsorption induced paramagnet and ferrimagnet in a porous layered magnet

Magnetic phases switch by not only solvents but also common ubiquitous gases such as oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2) is highly desired. Successful ESM by gas sorption was attained in $[\{Ru_2(2,4,6\text{-}F_3PhCO_2)_4\}_2TCNQ(OEt)_2]$ (**5**; 2,4,6-$F_3PhCO_2^-$ = 2,4,6-trifluorobenzoate). The compound **5** has a 1e-I form of $[D–A^––D^+]_\infty$, producing a strong intra-layer antiferromagnetic coupling between $[Ru_2^{II,II}]$ (S = 1) or $[Ru_2^{II,III}]$ (S = 3/2) and $TCNQ(OEt)_2^{\bullet-}$ (S = 1/2), as well as ferromagnetic interlayer interactions, induced the onset of long-range ferrimagnetic ordering at T_C = 110 K, which is the highest T_C among MOF magnet with sufficiently determined crystal structure. When CO_2 gas was adsorbed, **5** undergoes a structural phase transition involving an intra-lattice electron-transfer from A^- to D^+ to derive a paramagnetic N form of $[D–A–D]_\infty$ without magnetic phase transition due to the presence of diamagnetic A unit. The observed drastic change in the bulk-magnetization from a ferrimagnet (**5**) to a paramagnet (**5⊃CO_2**), namely, CO_2-induced demagnetization, as a result of ESM could be reversibly induced by CO_2 adsorption/desorption cycle. In addition, the electronic conductivity and permittivity are also affected by this CO_2-induced ESM.

Chapter 6. CO_2-adsorption induced antiferromagnet in a porous layered magnet

CO_2-induced antiferromagnet was demonstrated in **4**. Upon CO_2 adsorption, **4** is accompanied by a single-crystal to single-crystal transformation with ESM from 2e-I state (**4**) to 1e-I state (**4⊃CO_2**), and **4⊃CO_2** exhibit antiferromagnetic phase transition with T_N of 62 K. Owing to the reversible change of electronic states by the CO_2 adsorption/desorption processes, the magnetic phase is switched between paramagnetic phase (**4**) and antiferromagnetic phase (**4⊃CO_2**).

Chapter 7 Paramagnetic O_2 induced phase transition between ferrimagnet and antiferromagnet in a porous layered magnet

O_2-indicued magnetic phase switch from ferrimagnet to antiferromagnet was demonstrated in **3**. Compound **3** exhibits gas sorption capability for CO_2 and O_2. Spectroscopic studies revealed that no electronic state change was involved in the gas adsorption. Upon adsorption of CO_2, T_c decreased from 30 K to 24 K while ferrimagnetic order was maintained. In contrast, the uptake of paramagnetic O_2 molecules reveals the change of magnetic ordering from a ferrimagnet (T_c = 30 K) to an antiferromagnet (T_N = 30 K) without significant structural change.

The observed T_c change by CO_2 sorption is due to gas-induced structural modification, i.e., the modification of magnetic pathways. Whereas, the paramagnetic O_2 induced a switching of magnetic ordering, which may be explained by the magnetic interaction between O_2 and framework to lead the formation of new magnetic pathways. Such O_2-spin-sensitive porous magnet is scarce; this is the second example.

Chapter 8. Conclusion

In this thesis, the drastic modulation or the phase switching of bulk-magnetization in D/A-MOFs based on the ESM by guest accommodation were demonstrated (Chapter 2−6). In Chapter 7, the second example of the magnetic phase switching utilizing spin of paramagnetic O_2 gas and framework was demonstrated. As a chemical stimuli, not only organic solvent vapors (chapter 2-4), but also ubiquitous gases, such as CO_2 (chapter 5−7) and O_2 (chapter 7) could be applicable. The compound in chapter 2 is the first example that demonstrates ESM-induced drastic T_c switch. Chapter 3 indicates that weak host-guest interaction such as hydrogen bond can participate in ESM. Chapter 4 demonstrate the remarkable example of MOF-based magnet, where magnetic property of host framework can be variably tuned by guest molecule. The magnetization ON-OFF switch was for the first time realized by the accommodation of ubiquitous gas in chapter 5 and 6, not by paramagnetic gas in chapter 7, widening the method of magnetization control based on gas-sorption. These results provide new insights into the field of molecule-based magnet and promote the furthering development of stimuli-responsive materials.

別　紙

論文審査の結果の要旨

本学位論文では、化学的刺激により駆動する分子性デバイスの創製を目的に、水車型ルテニウム二核金属錯体（以下[Ru_2]と記す）と TCNQ 誘導体が、2：1 組成比で配位結合により集積化した二次元層状格子の電子状態および磁気物性について検討を行っている。特に、層状格子の電荷秩序状態と磁気秩序の溶媒蒸気やガス等のゲスト吸脱着のような“化学的刺激”に対する応答性に関する成果をまとめており、全８章から構成されている。

第１章は序論であり、本論文で用いる[Ru_2]-TCNQ 系二次元層状格子の取り得る多彩な電子状態と、それぞれが示す磁気物性の特徴について述べ、「外部刺激により電子状態を変化させることで磁気物性を大きく変化させる」という本論文全体に通じる戦略について説明している。第２章では、溶媒蒸気の吸脱着に伴い、70 K におよぶ大幅な磁気相転移温度（T_c）の変化を示す集積体について報告している。この大きな相転移温度変化は、TCNQ 分子の構造変化にも関係する格子の電子状態変化が原因だと結論づけている。第３章では、第２章と同様に、溶媒蒸気の吸脱着により、電子状態変化を伴い大幅な T_c 変化を示す集積体について報告しているが、前章とは異なり電子状態変化の一因が溶媒分子と格子の水素結合であることを論じている。第４章では、溶媒の吸脱着により、常磁性体とフェリ磁性体/反強磁性体の間でスイッチする集積体を報告しており、同じホスト骨格に対し、吸着させる溶媒蒸気の種類に応じて磁気秩序が制御可能であることを実証している。第５章では、反磁性ガスである CO_2 の吸脱着によっても電子状態変化を引き起こし、フェリ磁性体と常磁性体間での磁化の ON-OFF が可能であることを報告している。第６章では、CO_2 の吸脱着により、常磁性体と反強磁性体間の磁気秩序変化を示す集積体について報告している。第７章では、O_2 の吸着によりフェリ磁性体と反強磁性体間の磁気秩序変化を示す集積体について報告している。このような酸素ガスのスピンを感じる多孔性磁石は非常に稀である。第８章では本研究を通じて得られた新たな知見、“電子状態制御を通じた磁気物性制御”について総括し、今後の展望について述べている。

以上、本論文は著者が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、張俊提出の博士論文は、博士（理学）の学位論文として合格と認める。